

PREPARATION AND POLYMERIZATION OF ACRYLIC ESTERS
OF OLEFINIC ALCOHOLS

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In connection with projects (1) concerned with the production and subsequent cross-linkage of unsaturated acrylic resins, various monomers containing two or more olefinic linkages were required. This paper describes the preparation of several alkenyl acrylates that seemed suitable for the preparation of soluble unsaturated acrylic copolymers because of the presence of the highly polymerizable acrylate double bond and the relatively unreactive olefinic linkages of the alkoxyl groups. There is little published information on alkenyl acrylates (2, 3), but several alkenyl methacrylates, including the allyl (3), methallyl (3, 4), oleyl (4), furfuryl (5), *alpha*-triphenylmethallyl (6), and vinyl (7, 8, 9) esters, have been prepared.

The alcoholysis method was found useful in the present work for making alkenyl acrylates, but the yields (Table I) were generally lower than those obtained in the preparation of alkyl acrylates (10).

The allyl (3), methallyl (3), and the *beta*-chloroallyl acrylates were prepared also by pyrolysis of the corresponding *alpha*-acetoxypromionates, but the yields were low. Negligible yields of crotyl and methyl vinyl carbinyl acrylates were obtained in the pyrolysis of the corresponding acetoxypromionates, but butadiene was formed in high yields from both esters.

The relative tendencies of the alkenyl acrylates to form insoluble (presumably cross-linked) copolymers with methyl acrylate were estimated by polymerizing various percentages of the ester with methyl acrylate in ethyl acetate and comparing the minimum concentration of alkenyl acrylate required to produce gelation of the copolymer solution. The most active monomers were the methallyl and *beta*-chloroallyl acrylates, whereas crotyl acrylate had the least tendency to cause gelation (Table II). Although 0.1% of methallyl acrylate produced gelation, approximately forty times as much of the isomeric crotyl acrylate was required. Whether the alkenyl acrylates would have the same relative gelling effects when polymerized with monomers other than methyl acrylate was not determined.

Several of the ethyl acetate solutions containing soluble copolymers (Table II) were used to prepare cross-linked films. Benzoyl peroxide (2 to 5% of the copolymer) was dissolved in the solution. The viscous solution was applied to a flat surface, and the solvent was allowed to evaporate. The resulting films as such could be readily redissolved in organic solvents. After being heated at about 80° for a short time, however, the films were insoluble. It was observed that similar treatment of polymerized alkyl acrylates, that is, acrylic resins containing no olefinic unsaturation, also yielded insoluble films.

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TABLE I
OLEFINIC ESTERS OF ACRYLIC ACID

ESTER	YIELD % ^a	CONVERSION, % ^b	METHYL ACRYLATE LOST, %	B.P. °C.	PRESS., MM	n_D^{20}	d_4^{20}	MOL. REFRACTION		SAP. EQUIV.	
								Calc'd ^c	Found	Calc'd	Found
Allyl.....	70	70	—	47	40	1.4320	0.9441	30.63	30.80	112.1	112.4
beta-Methallyl.....	74	56	2	68	50	1.4372	.9285	35.25	35.60	126.1	128.3
Methyl vinyl carbinyld.....	37	27	1	70	97	1.4299	.9066	35.25	35.94	126.2	128.2
Crotyl.....	69	59	10	60	23	1.4422	.9344	35.25	35.73	126.2	128.5
beta-Chloroallyl.....	56	33	—	72	29	1.4600	1.1243	35.50	35.70	146.6	140.5
gamma-Chloroallyl.....	68	34	27	87	34	1.4680	1.1385	35.50	35.79	146.6	146.0
4-Methyl-4-penten-2-yl.....	70	40	9	62	14	1.4380	0.9027	44.48	44.85	154.2	151.2
Citronellyld.....	91	90	27	108	5.4	1.4500	.8879	62.95	63.66	210.3	216.6
Geranyl.....	64	59	13	116	6.2	1.4690	.9121	62.49	63.60	208.3	212.4
Rhodinyld.....	80	79	18	107	4.2	1.4591	.9026	62.95	63.71	210.3	214.4
Cinnamyl.....	71	52	13	108	1.2	1.5508 ^e	1.0495 ^e	54.74	57.20	188.2	191.8
Furfuryl.....	86	86	17	93	16	1.4800	1.1125	38.84	38.85	152.1	150.9

^a On basis of unrecovered alcohol.

^b On basis of total alcohol used.

^c No correction was made for the exaltation owing to conjugated double bonds.

^d The purity of this sample is questionable, since separation of the alcohol from the ester was difficult.

^e At 25°.

TABLE II
GELATION OF COPOLYMERS OF METHYL ACRYLATE

EXPT. NO.	POLYFUNCTIONAL MONOMER	CONCENTRATION, % OF TOTAL MONOMER	
		No gel formed	Gel formed
1	beta-Methallyl acrylate	0.05	0.10
2	beta-Chloroallyl acrylate	.05	.10
3	Allyl acrylate	.10	.20
4	beta-Methallyl methacrylate	.10	.20
5	Cinnamyl acrylate	.10	.20
6	4-Me.-4-penten-2-yl acrylate	.10	.20
7	alpha-Carballyloxyethyl acrylate ^a	.10	.20
8	gamma-Chloroallyl acrylate	.10	.20
9	Allyl methacrylate	.20	.30
10	Geranyl acrylate	.30	.50
11	CR-39 monomer ^b	.50	.80
12	Furfuryl acrylate	1.00	2.00
13	Rhodinyl acrylate	2.00	3.00
14	Citronellyl acrylate	2.00	3.00
15	Bis-(allyl lactate) maleate ^c	2.00	5.00
16	Crotyl acrylate	3.00	4.00

^a Preparation and physical properties described in another paper, Rehberg, Dixon, and Fisher, *J. Am. Chem. Soc.*, **67**, 208 (1945).

^b Additional data on this allyl monomer $[O(CH_2CH_2OCOOCH_2CH:CH_2)_2]$ have been given by Coles, Deuberry, and Curry, *J. Optical Soc. Am.*, **34**, (10), 623 (Oct. 1944) and by Pechukas, Strain, and Dial, *Modern Plastics*, **20**, 101 (1943).

^c Prepared in a separate investigation; will be described in a later publication.

EXPERIMENTAL

Preparation of monomeric esters. The acrylic esters (Table I) were prepared by the alcoholysis of methyl acrylate, using essentially the procedure described previously (10). One important variation from that procedure was the use of alkaline catalysts and polymerization inhibitors in experiments in which there appeared to be danger that mineral acid would cause polymerization, isomerization, or decomposition of the olefinic alcohol or its ester. Aluminum alcoholate was the preferred catalyst and phenyl-*beta*-naphthylamine was used as polymerization inhibitor when the alcoholate was used as catalyst. Com-

TABLE III
PHYSICAL CONSTANTS OF OLEFINIC ALCOHOLS

ALCOHOL	BOILING POINT, °C. (MM.)		REFRACTIVE INDEX, n_D^{20}		SOURCE
	Observed	Literature	Observed	Literature	
Allyl.....	97	96.9 ^a	1.4134	1.4135 ^a	Shell Chemical Corp.
Methallyl.....	114	114.5 ^a	1.4255	1.4255 ^a	" " "
<i>beta</i> -Chloroallyl ...	133-134	134 ^a	—	1.460 ^a	" " "
<i>gamma</i> -Chloroallyl.	147-149	147-153 ^a	1.4655	—	" " "
Crotyl.....	122-123	123 ^a	1.4300	1.430 ^a	" " "
Me. vinyl carbiny.	97	97 ^a	—	1.415 ^a	" " "
4-Me.-4-penten-2-yl.....	40/13	—	1.4330	—	" " "
Geranyl.....	132/27	129/25 ^b	1.4760	1.4766 ^c	Eastman Kodak Co., (Tech. grade)
Citronellyl.....	105/10	106-108/12 ^d	1.4522	1.4566 ^b	Eastman Kodak Co. (White Label)
Rhodiny.	114/15	118-119.5/18 ^e	1.4625	1.4588	Eastman Kodak Co.
	113-114/15	113-114/15 ^e		(15°) ^c	(Technical)
Cinnamyl.....	110-112/4	143-145/14 ^b	1.5835	1.5819 ^b	Eastman Kodak Co.
			(25°)		(Practical)
Furfuryl.....	—	83-84/25 ^f	1.4874	1.4868 ^f	Eastman Kodak Co., (White label)

^a Technical data supplied by Shell Chemical Corp.

^b Heilbron and Bunbury, "Dictionary of Organic Compounds," 1943, Oxford University Press, New York.

^c Simonsen, The Terpenes, Vol. I, 1931, The University Press, London.

^d Karrer, Geiger, Rentschler, Zbinden, and Kugler, *Helv. Chim. Acta*, 26, 1741 (1943).

^e Handbook of Chemistry & Physics, 27th Ed., 2553 pp. (1943), Chemical Rubber Publishing Co., Cleveland, Ohio.

^f Dunlop and Trimble, *Ind. Eng. Chem.*, 32, 1000 (1940).

mercially available aluminum isopropoxide was satisfactory, though in a few experiments amalgamated aluminum foil was dissolved in the olefinic alcohol at the beginning of the experiment. Allyl and *beta*-chloroallyl acrylates were prepared with sulfuric acid as catalyst, but in all the other experiments aluminum alcoholate was used.

No attempt was made to determine whether double bonds migrated during the alcoholysis, but Day (11) prepared alkenyl esters by alcoholysis in the presence of aluminum alcoholate, hydrolyzed the resulting esters, examined the olefinic alcohols, and found that little or no migration had occurred. Redistilled samples of alcohols were used in the alcoholysis experiments. The sources of the alcohols and physical constants of the redistilled samples are given in Table III.

Allyl(3), methallyl(3), and *beta*-chloroallyl acrylates and allyl and methallyl methacrylates were prepared by pyrolysis of the corresponding *alpha*-acetoxypionates and *alpha*-acetoxisobutyrate, respectively. We have greatly improved the yield of allyl and methallyl lactates and simplified the procedure for their preparation. The following procedure has consistently produced 90% conversion to the allyl ester in a single treatment of lactic acid with allyl alcohol.

Direct esterification of lactic acid. Ten moles (1125 g.) of 80% edible lactic acid, 400 cc. of benzene, and 5 cc. of sulfuric acid were refluxed in a still having a 3-foot column fitted with a water trap at its top, water being drawn off as it collected (300 cc. in 5 hr.). When production of water became slow, 40 moles (2323 g.) of allyl alcohol was added and refluxing continued, with removal of water (220 cc., containing some allyl alcohol, in 20 hr.). When no more water was produced, the flask was cooled, 20 g. of anhydrous sodium acetate was added to neutralize the sulfuric acid, and the benzene was distilled at atmospheric pressure as its azeotrope with allyl alcohol. The remainder of the alcohol was then distilled fairly

TABLE IV
MONO- AND DI-ESTERS OF LACTIC ACID

ESTER	YIELD, %	B.P., °C.	PRESS., MM.	n_D^{20}	d_4^{20}	MOL. REFRACTION		SAP. EQUIV.	
						Calc'd	Found	Calc'd	Found
ALKENYL LACTATES									
<i>beta</i> -Chloroallyl	76	83	5	1.4627	1.2153	37.49	37.28	164.6	163.2
<i>gamma</i> -Chloroallyl	65	106	12	1.4670	1.2166	37.49	37.54	164.6	161.9
Crotyl ^a	83	92	18	1.4420	1.0106	37.24	37.75	144.2	149.3
Methyl vinyl carbinyl.....	77	58	8	1.4326	1.0091	37.24	37.10	144.2	144.5
ALKENYL <i>alpha</i> -ACETOXYPROPIONATES									
<i>beta</i> -Chloroallyl	84	96	5	1.4460	1.1792	46.85	46.73	103.3	102.0
Crotyl ^a	86	94	8	1.4347	1.0338	46.60	46.97	93.1	95.1
Methyl vinyl carbinyl.....	100	80	8	1.4256	1.0233	46.60	46.59	93.1	93.2

^a This ester was not pure; the nature of the impurities is not known.

rapidly under about 50 mm. pressure, after which the allyl lactate was rapidly distilled at 60° (7 mm.). The yield was 1178 g., or 90.5%.

With the procedure described above, *beta*-chloroallyl lactate was prepared in 76% yield. Methyl vinyl carbinol and crotyl alcohol appeared to be somewhat unstable in the presence of sulfuric acid, so for the preparation of their lactates the foregoing procedure was modified somewhat. The lactic acid, alcohol, and benzene were mixed and refluxed with removal of water until little water was produced. Then 10 g. of *p*-toluenesulfonic acid was added, and heating continued. When no more water was produced, the catalyst was neutralized and the product distilled as described above.

Alcoholysis of lactic esters. Methallyl and *gamma*-chloroallyl lactates were prepared by alcoholysis of methyl or ethyl lactate. Three moles (312 g.) of methyl lactate, 6 moles (555 g.) of *gamma*-chloroallyl alcohol, and 10 g. of aluminum *tert*-butoxide were mixed and refluxed in a still, from which methanol was withdrawn as fast as it collected at the still-head. When production of methanol ceased, the excess alcohol was distilled at 54° (13 mm.), after which the product was obtained at 105° (12 mm.); yield, 65%. This procedure, using methallyl alcohol, gave a 70% yield of methallyl lactate.

Acetylation of alkenyl lactates. All the alkenyl *alpha*-acetoxypionates (Table IV) were prepared by using a slight excess of acetic anhydride with the appropriate lactate.

Pyrolysis of alkenyl alpha-acetoxypropionates. The apparatus and procedure previously described(3) for the pyrolysis of allyl and methallyl *alpha*-acetoxypropionates and *alpha*-acetoxyisobutyrate were used in the pyrolysis of *beta*-chloroallyl, crotyl, and methyl vinyl carbonyl *alpha*-acetoxypropionates. As was expected, the principal products obtained by the pyrolysis of the two latter esters were butadiene, acetic acid, acetaldehyde, and carbon monoxide, little of the corresponding acrylic esters being produced. *β*-Chloroallyl *alpha*-acetoxypropionate gave a fair yield of the acrylate; other products were not identified (Table V).

Because of the discouraging results from the other esters, *gamma*-chloroallyl lactate was not acetylated and pyrolyzed.

Determination of gelation tendency. In each experiment, 20 g. of methyl acrylate and 0.05 g. of benzoyl peroxide were dissolved in 80 g. of ethyl acetate, and the desired percentage of the polyfunctional monomer, based on the total mixture of monomers, was added. The flask containing the mixture was then fitted with an upright condenser and placed in a bath, which was kept at 60° for 24 hours and then at 80° for another 24 hours. The contents of the flasks were then examined for evidence of gelation. The products ranged from sirupy solutions to firm, elastic, solid gels. When the solutions could be poured from the flasks, even though they were sometimes ropy or stringy, they were recorded as not gelled.

TABLE V
PYROLYSIS OF ALKENYL *alpha*-ACETOXYPROPIONATES

ESTER	TEMP., °C.	CONTACT TIME, SEC. ^a	% CRACKED	ACRYLATE	
				Yield, % ^b	Conversion, % ^c
<i>beta</i> -Chloroallyl.....	525	9.7	68	43	29
Crotyl.....	500	8.5	85	5	4
Methyl vinyl carbonyl.....	525	9.1	87	7	6

^a Based on free space in the heated zone of the Pyrex-glass pyrolysis tube.

^b On basis of unrecovered ester.

^c On basis of total ester used.

The lowest tested concentrations of cross-linking comonomers which produced gelation and the highest tested concentrations which failed to produce gelation are shown in Table II. On the basis of earlier work(12, 13), it seems likely that results different from those of Table II would have been obtained in solutions of higher or lower concentration and at different temperatures and catalyst concentrations. The present tests were made under uniform conditions, however, and the results of Table II should represent the relative tendencies of the monomers to form cross-linked polymers.

Mass polymerization. The monomers were placed in elongated Pyrex-glass test tubes (approximately 6 mm. I.D. and 200 mm. long), and the end of the tube was sealed. Small quantities of benzoyl peroxide were included in some experiments. The resulting ampoules were allowed to stand at room temperature until polymerization occurred. The polymers were transparent, infusible, and insoluble. All were hard and strong except the citronellyl, rhodiny, geranyl, and cinnamyl polymers, which were elastic and gel-like and had little strength.

SUMMARY

The acrylic esters of allyl, methallyl, methyl vinyl carbonyl, crotyl, *beta*-chloroallyl, *gamma*-chloroallyl, methylpentenyl, citronellyl, geranyl, rhodiny, cinnamyl, and furfuryl alcohols were prepared by alcoholysis of methyl acrylate.

Polymerization of these alkenyl acrylates yielded insoluble, cross-linked resins. When copolymerized with methyl acrylate, methallyl and *beta*-chloroallyl acrylates had the greatest tendency to form cross-linked polymers and crotyl acrylate had the least.

The preparation and pyrolysis of *beta*-chloroallyl, crotyl, and methyl vinyl carbiny acetoxypionates are described.

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